

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-048818

(43)Date of publication of application : 18.02.2000

AG

(51)Int.Cl.

H01M 4/58

H01M 4/02

H01M 10/40

(21)Application number : 10-225439

(71)Applicant : SEIDOU KAGAKU KOGYO KK

(22)Date of filing : 24.07.1998

(72)Inventor : YOSHIKAWA CHIKAHITO

WAKE YUMIKO

MAHANA AIKO

(54) POSITIVE ELECTRODE ACTIVE MATERIAL AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode active material with a cycle life characteristic superior in charging/discharging and a nonaqueous electrolyte secondary battery using it.

SOLUTION: This positive electrode active material is represented by the expression  $\text{Li}_{1+x}\text{Mn}_{2-x-y-z}\text{A}_y\text{B}_z\text{O}_4$ , and this nonaqueous electrolyte secondary battery uses it. In the expression A is at least one element selected from Co, Ni, Fe and Cr, B is at least one element selected from Mg and Ca and x, y and z are set in the respective ranges of  $0 \leq x \leq 0.09$ ,  $0.01 \leq y \leq 0.3$ ,  $0.01 \leq z \leq 0.3$ .

## LEGAL STATUS

[Date of request for examination] 24.07.1998

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number] 2963452

[Date of registration] 06.08.1999

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right] 04.01.2001

Copyright (C); 1998,2003 Japan Patent Office

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2000-48818

(P2000-48818A)

(43) 公開日 平成12年2月18日 (2000.2.18)

(51) Int.Cl. <sup>7</sup>	識別記号	F I	ターマコード* (参考)
H 0 1 M 4/58		H 0 1 M 4/58	5 H 0 0 3
4/02		4/02	C 5 H 0 1 4
10/40		10/40	Z 5 H 0 2 9

審査請求 有 請求項の数 2 F D (全 5 頁)

(21) 出願番号	特願平10-225439	(71) 出願人	593078615 正同化学工業株式会社 大阪府大阪市中央区北浜二丁目1番26号
(22) 出願日	平成10年7月24日 (1998.7.24)	(72) 発明者	吉川 周仁 兵庫県赤穂市中広1576 正同化学工業株式 会社内
		(72) 発明者	和氣 由美子 兵庫県赤穂市中広1576 正同化学工業株式 会社内
		(74) 代理人	100081536 弁理士 田村 巖

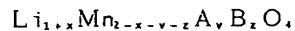
最終頁に続く

(54) 【発明の名称】 正極活物質及びこれを用いた非水電解液二次電池

(57) 【要約】

【課題】 充放電でのサイクル寿命特性の優れた正極活物質及びこれを用いた非水電解液二次電池を提供する

【解決手段】 下記式で表される正極活物質及びこれを用いた非水電解液二次電池。



A = Co, Ni, Fe, Cr から選ばれる少なくとも1つの元素

B = Mg, Zn, Ca から選ばれる少なくとも1つの元素

$0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$

【特許請求の範囲】

【請求項1】 下記式で表される正極活物質、



A=Co, Ni, Fe, Crから選ばれる少なくとも1つの元素

B=Mg, Zn, Caから選ばれる少なくとも1つの元素

$0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$

【請求項2】 請求項1の正極活物質を用いる非水電解液二次電池。

【発明の詳細な説明】

【0001】

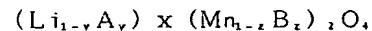
【発明の属する技術分野】 本発明は改良された正極活物質、これを用いた非水電解液二次電池に関する。

【0002】

【従来の技術】 非水電解液二次電池は、例えば負極にリチウム、リチウム化合物、リチウム合金等を用い、電解液として炭酸プロピレン(PC)、1,2-ジメトキシエタン(DME)、 $\gamma$ -ブチロラクトン( $\gamma$ -BL)、テトラヒドロフラン(THF)などの非水溶媒中にLiClO<sub>4</sub>、LiBF<sub>4</sub>、LiAsF<sub>6</sub>、LiPF<sub>6</sub>等のリチウム塩を溶解した非水電解液を用い、正極活物質としては主にTiS<sub>2</sub>、MoS<sub>2</sub>、V<sub>2</sub>O<sub>5</sub>、V<sub>6</sub>O<sub>13</sub>等の遷移金属の硫化物または酸化物を用いている。一方、非水電解液一次電池に用いられているMnO<sub>2</sub>は、低コストであるという利点から、これを二次電池の正極活物質として用いることが考えられ、中でもスピネル構造のLiMn<sub>2</sub>O<sub>4</sub>は充放電の可逆性を有することが報告されている。

【0003】

【発明が解決しようとする課題】 しかしながら上述したLiMn<sub>2</sub>O<sub>4</sub>を正極活物質として用いた二次電池では、充放電でのサイクル寿命特性が劣るという問題があった。これを解決するために、例えば特開平2-139861号に



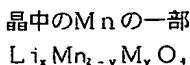
A=Na, K, Cu, Ag, Znから選ばれる元素

B=V, Cr, Fe, Co, Niから選ばれる元素

$0.9 \leq x \leq 1.1$ 、 $0.0 \leq y \leq 0.2$ 、 $0.0 \leq z \leq 0.2$

で表される正極活物質、特開平3-108261号にLiMn<sub>2</sub>O<sub>4</sub>に2価金属イオン(例えばMg, Ca, Zn, Cd)を添加した正極活物質、

【0004】 特開平4-160769号にLiMn<sub>2</sub>O<sub>4</sub>結晶中のMnの一部をCoで置換し、



M=Co, Ni, Fe, Crから選ばれる少なくとも1種の元素

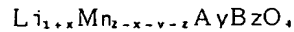
$0.85 \leq x \leq 1.15$ 、 $0.3 < y \leq 0.5$ で表される正極活物質が提案されており、いずれもその充放電でのサイ

クル寿命特性は改良されているが尚、十分ではなかつ

た。本発明の課題は充放電でのサイクル寿命特性の優れた正極活物質及びこれを用いた非水電解液二次電池を提供することにある。

【0005】

【課題を解決するための手段】 本発明は下記式で表される正極活物質及びこれを用いた非水電解液二次電池に係る。



A=Co, Ni, Fe, Crから選ばれる少なくとも1つの元素

B=Mg, Zn, Caから選ばれる少なくとも1つの元素

$0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$

【0006】

【発明の実施の形態】 本発明の上記式で表される正極活物質の製法の1例を以下に示す。例えば、Li<sub>1-x</sub>Mn<sub>2-x-y-z</sub>Co<sub>y</sub>Mg<sub>z</sub>O<sub>4</sub>で表される化合物は、Li化合物、Mn化合物、Co化合物、Mg化合物を所定の組成になるよう混合し、この混合物を加熱処理することにより得られる。ここでLi化合物としては、例えばLi<sub>2</sub>CO<sub>3</sub>、LiOH・H<sub>2</sub>O、LiNO<sub>3</sub>等を、Mn化合物としては、例えばMnO<sub>2</sub>、Mn<sub>2</sub>O<sub>3</sub>、MnCO<sub>3</sub>等を、Co化合物としては、例えばCo<sub>2</sub>O<sub>3</sub>、CoCO<sub>3</sub>、Co(OH)<sub>2</sub>等を、Mg化合物としては、例えばMgO、Mg(OH)<sub>2</sub>等を挙げることができる。加熱温度は通常約650~1000℃の範囲であるが、750~900℃の場合、さらに良好なサイクル寿命が得られるので好ましい。

【0007】 ここでA=Co, Ni, Fe, Crから選ばれる少なくとも1つの元素、B=Mg, Zn, Caから選ばれる少なくとも1つの元素であるが、これらのうち特にA=Co, B=Mgが好ましい。また $0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$ の範囲から選ばれるが、このうち $0 \leq x \leq 0.06$ 、 $0.05 \leq y \leq 0.3$ 、 $0.05 \leq z \leq 0.3$ の範囲が好ましく、特に $0 \leq x \leq 0.03$ 、 $0.1 \leq y \leq 0.2$ 、 $0.1 \leq z \leq 0.2$ の範囲が好ましい。

【0008】 本発明においては、上記正極活物質を用いて非水電解液二次電池を作成することができる。この非水電解液二次電池において、負極、電解液としては通常従来使用されているものを用いることができる。例えば負極としてはリチウム、リチウム化合物、リチウム合金、カーボン等を、電解液としてエチレンカーボネート(EC)、ジエチレンカーボネート(DEC)、炭酸プロピレン(PC)、1,2-ジメトキシエタン(DME)、 $\gamma$ -ブチロラクトン( $\gamma$ -BL)、テトラヒドロフラン(THF)などの非水溶媒中にLiClO<sub>4</sub>、LiBF<sub>4</sub>、LiAsF<sub>6</sub>、LiPF<sub>6</sub>等のリチウム塩を溶解した非水電解液を用いることができる。

【0009】 非水電解液二次電池の作成方法も通常従来使用されている方法をそのまま採用することができる。

本発明の上記正極活物質を用いて得られた非水電解液二次電池は優れた充放電でのサイクル寿命特性を有するもので、そのサイクル寿命は以下の実施例及び比較例より明らかなように、 $\text{LiMn}_2\text{O}_4$ の約6倍、 $\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$ 、 $\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$ 、 $\text{LiMn}_{1.7}\text{Co}_{0.3}\text{O}_4$ の約1.58～1.64倍、更には2倍以上の顕著な効果を有する。

【0010】

【実施例】以下に実施例および比較例を挙げて本発明を説明する。

実施例1～6および比較例1～7

$\text{Li}_2\text{CO}_3$ 、電解-Mn $\text{O}_2$ 、 $\text{Co}_3\text{O}_4$ 、 $\text{MgO}$ を所定の組成になるように秤量した後、乳鉢にて混合し、900℃で12時間焼成して表1に示される材料を合成した。得られた材料を粉末X線回折したところ図1、2に示されるように、 $\text{LiMn}_2\text{O}_4$ 相が存在することが確認できた。さらに、材料0.8g、アセチレンブラック0.13g、ポリテトラフルオロエチレン0.07gを乳鉢にて混練し、厚さ30μmまで圧延した後、Niメッシュ(60mesh)に圧着させ、150℃、12時間の真空乾燥を行い、電池サイクル試験に用いた。電解液には1M  $\text{LiClO}_4$ +50%エチレンカーボネイト(EC)+50%ジメ

\*エチレンカーボネイト(DEC)を、対極および参照極にはNiメッシュ(60mesh)上にLi箔を圧着させたものを用いた。図3に電池試験に用いたセルを示す。電位範囲3.3～4.3V vs.  $\text{Li}^+/\text{Li}$ 、電流値は試料1g当たり49.4mA、温度は25℃とした。

【0011】表1に充放電サイクル寿命を示す。 $\text{LiMn}_2\text{O}_4$ 中のMnの一部をCoもしくはMgで置換しその置換量が増すごとにサイクル寿命が大きくなることが分かる。しかしCoとMgの2元素を同時に置換することにより、CoもしくはMgの1元素のみ置換した材料に比べさらにサイクル寿命が大きくなることが分かる。さらに、CoとMgの2元素を同時に置換した材料に、Li置換することにより、さらにサイクル寿命が大きくなることが分かる。このように、 $\text{LiMn}_2\text{O}_4$ 中のMnの一部を1元素単独で置換を行うよりも、CoとMgの2元素、もしくはLi、Co、Mgの3元素で同時に置換することによりさらにサイクル寿命が向上することが分かる。尚、サイクル寿命は1サイクル目の放電容量の80%に減少したときの寿命とし、そのサイクル数をいう。

【0012】

【表1】

		組 成	サイクル寿命 (サイクル数)
比 較 例	1	$\text{LiMn}_2\text{O}_4$	92
	2	$\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$	58
	3	$\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$	250
	4	$\text{LiMn}_{1.7}\text{Co}_{0.3}\text{O}_4$	320
	5	$\text{LiMn}_{1.9}\text{Mg}_{0.1}\text{O}_4$	75
	6	$\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$	265
	7	$\text{LiMn}_{1.7}\text{Mg}_{0.3}\text{O}_4$	332
実 施 例	1	$\text{LiMn}_{1.9}\text{Co}_{0.05}\text{Mg}_{0.05}\text{O}_4$	525
	2	$\text{LiMn}_{1.8}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	600以上
	3	$\text{LiMn}_{1.7}\text{Co}_{0.15}\text{Mg}_{0.15}\text{O}_4$	600以上
	4	$\text{Li}_{1.02}\text{Mn}_{1.88}\text{Co}_{0.05}\text{Mg}_{0.05}\text{O}_4$	600以上
	5	$\text{Li}_{1.06}\text{Mn}_{1.74}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	600以上
	6	$\text{Li}_{1.09}\text{Mn}_{1.71}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	600以上

【0013】

【発明の効果】本発明では充放電でのサイクル寿命特性の優れた正極活物質及びこれを用いた非水電解液二次電池を提供することができる。

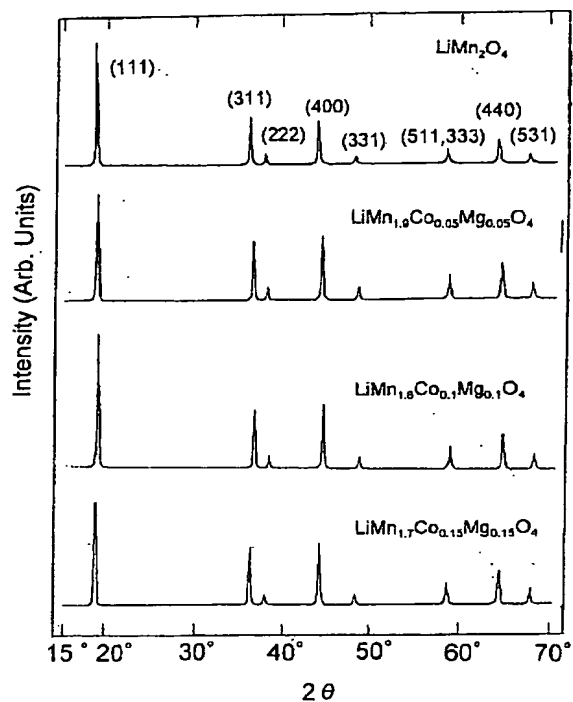
【図面の簡単な説明】

40 【図1】  $\text{LiMn}_2\text{O}_4$ および実施例1～3で得られた正極活物質のX線回折図である。

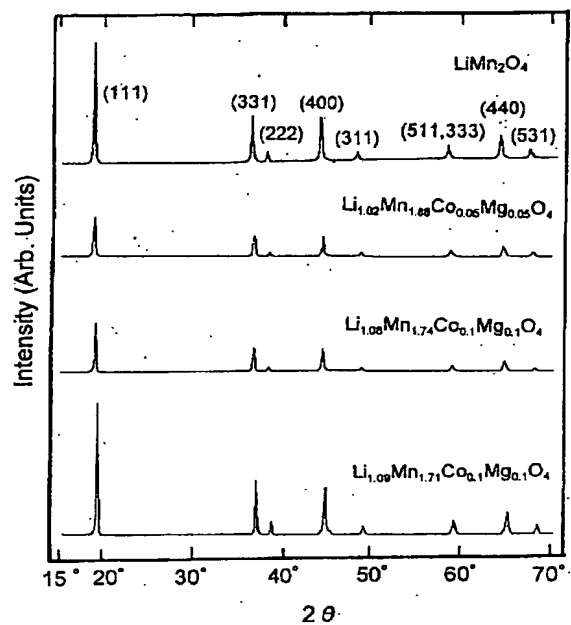
【図2】  $\text{LiMn}_2\text{O}_4$ および実施例4～6で得られた正極活物質のX線回折図である。

【図3】 充放電サイクル試験に用いたセルを示す。

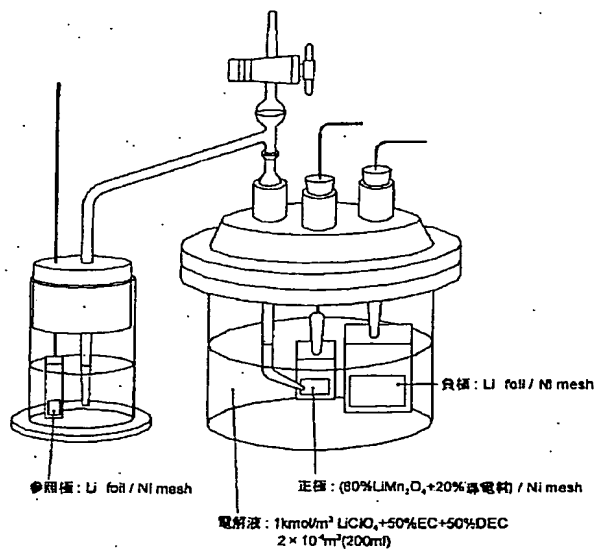
【図1】



【図2】



【図3】



【手続補正書】

【提出日】平成11年6月7日(1999. 6. 7)

【手続補正1】

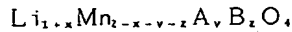
【補正対象書類名】明細書

【補正対象項目名】請求項1

【補正方法】変更

【補正内容】

【請求項1】 下記式で表される正極活物質。



A=Co, Ni, Fe, Crから選ばれる少なくとも1つの元素

B=Mg, Caから選ばれる少なくとも1つの元素

$0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$

【手続補正2】

【補正対象書類名】明細書

【補正対象項目名】0005

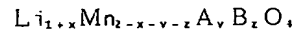
【補正方法】変更

【補正内容】

【0005】

【課題を解決するための手段】本発明は下記式で表される正極活物質及びこれを用いた非水電解液二次電池に係\*

＊る。



A=Co, Ni, Fe, Crから選ばれる少なくとも1つの元素

B=Mg, Caから選ばれる少なくとも1つの元素

$0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$

【手続補正3】

【補正対象書類名】明細書

【補正対象項目名】0007

【補正方法】変更

【補正内容】

【0007】ここでA=Co, Ni, Fe, Crから選ばれる少なくとも1つの元素、B=Mg, Caから選ばれる少なくとも1つの元素であるが、これらのうち特にA=Co, B=Mgが好ましい。また $0 \leq x \leq 0.09$ 、 $0.01 \leq y \leq 0.3$ 、 $0.01 \leq z \leq 0.3$ の範囲から選ばれるが、このうち $0 \leq x \leq 0.06$ 、 $0.05 \leq y \leq 0.3$ 、 $0.05 \leq z \leq 0.3$ の範囲が好ましく、特に $0 \leq x \leq 0.03$ 、 $0.1 \leq y \leq 0.2$ 、 $0.1 \leq z \leq 0.2$ の範囲が好ましい。

フロントページの続き

(72)発明者 真▲はな▼ 愛子

兵庫県赤穂市中広1576 正同化学工業株式会社内

Fターム(参考) 5H003 AA04 BB05 BD00

5H014 AA02 HH00

5H029 AJ05 AK03 AL12 AM05 AM07

BJ01 HJ02

JAPANESE

[JP,2000-048818,A]

AG

---

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

CLAIMS

---

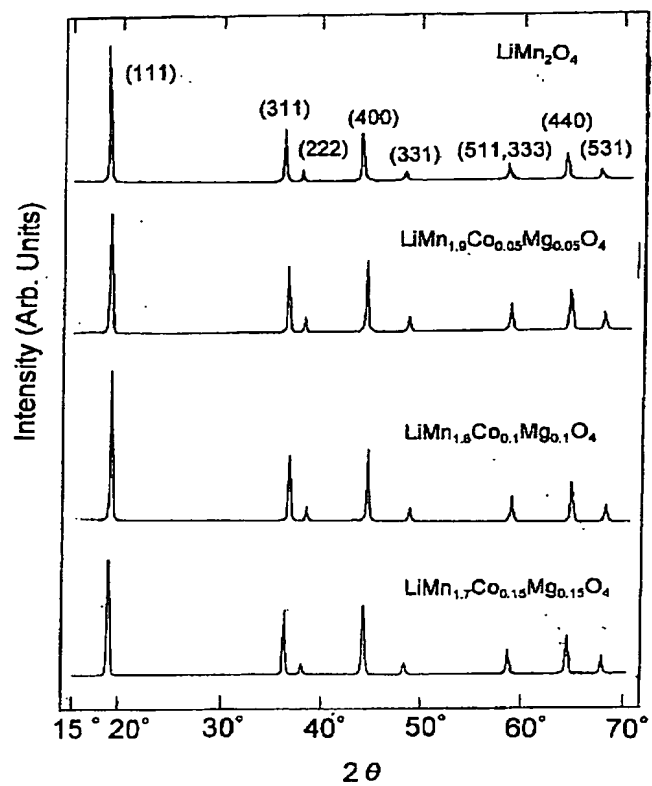

[Claim(s)]

[Claim 1] The positive active material expressed with the following formula.

$\text{Li}_{1+x}\text{Mn}_{2-x-y-z}\text{A}_y\text{B}_z\text{O}_4$  A=Co, at least one element B=Mg chosen from nickel, Fe, and Cr, at least one element  $0 \leq x \leq 0.09$  chosen from Zn and calcium,  $0.01 \leq y \leq 0.3$ ,  $0.01 \leq z \leq 0.3$ . [Claim 2] The nonaqueous electrolyte rechargeable battery using the positive active material of a claim 1.

---

[Translation done.]

Drawing selection drawing 1 

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which were improved.

[0002]

[Description of the Prior Art] A nonaqueous electrolyte rechargeable battery uses a lithium, a lithium compound, a lithium alloy, etc. for a negative electrode. As the electrolytic solution, a propylene carbonate (PC), 1, 2-dimethoxyethane (DME), The nonaqueous electrolyte which dissolved the lithium salt of  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{LiPF}_6$  grade is used into non-aqueous solvents, such as gamma-butyrolactone (gamma-BL) and a tetrahydrofuran (THF). As a positive active material, the sulfide or oxide of transition metals of  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{V}_6\text{O}_{13}$  grade is mainly used. On the other hand, from the advantage that  $\text{MnO}_2$  used for the nonaqueous electrolyte primary cell is a low cost, it is possible to use this as a positive active material of a rechargeable battery, and it is reported especially that  $\text{LiMn}_2\text{O}_4$  of Spinel structure has the reversibility of charge and discharge.

[0003]

[Problem(s) to be Solved by the Invention] However, in the rechargeable battery using  $\text{LiMn}_2\text{O}_4$  mentioned above as a positive active material, there was a problem that the cycle-life property in charge and discharge was inferior. In order to solve this To for example, JP,2-139861,A The positive active material expressed with  $x(\text{Mn}_{1-z}\text{Bz})_2\text{O}_4$   $\text{A}=\text{Na}$ , element  $\text{B}=\text{V}$  chosen from K, Cu, Ag, and Zn, the element  $0.9 \leq x \leq 1.1$  chosen from Cr, Fe, Co, and nickel,  $0.0 \leq y \leq 0.2$ , and  $0.0 \leq z \leq 0.2$ , ( $\text{Li}_{1-y}\text{Ay}$ ) The positive active material, [0004] which added the divalent metallic ion (for example, Mg, calcium, Zn, Cd) to JP,3-108261,A at  $\text{LiMn}_2\text{O}_4$  A part of Mn under  $\text{LiMn}_2\text{O}_4$  crystal is replaced by JP,4-160769,A by Co, and it is from  $\text{Li}_x\text{Mn}_{2-y}\text{MyO}_4$   $\text{M}=\text{Co}$ , and nickel, Fe and Cr. At least one sort of elements  $0.85 \leq x \leq 1.15$  chosen and the positive active material expressed with  $0.3 < y \leq 0.5$  were proposed, and although all were improved, they were not in addition enough. [ of the cycle-life property in the charge and discharge ] The technical problem of this invention is to offer the nonaqueous electrolyte rechargeable battery using the positive active material and this which were excellent in the cycle-life property in charge and discharge.

[0005]

[Means for Solving the Problem] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which are expressed with the following formula.

$\text{Li}_{1+x}\text{Mn}_{2-x-y-z}\text{AyBzO}_4$   $\text{A}=\text{Co}$ , at least one element  $\text{B}=\text{Mg}$  chosen from nickel, Fe, and Cr, at least one element  $0 \leq x \leq 0.09$  chosen from Zn and calcium,  $0.01 \leq y \leq 0.3$ ,  $0.01 \leq z \leq 0.3$  [0006]

[Embodiments of the Invention] One example of the process of a positive active material expressed with the above-mentioned formula of this invention is shown below. For example, the compound expressed with  $\text{Li}_{1+x}\text{Mn}_{2-x-y-z}\text{CoyMgzO}_4$  mixes Li compound, Mn compound, Co compound, and Mg compound so that it may become predetermined composition, and it is obtained by heat-treating this mixture. here -- as Li compound --  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and  $\text{LiNO}_3$  grade -- as Mn compound --  $\text{MnO}_2$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnCO}_3$  grade -- as Co compound --  $\text{Co}_3$  -- as a Mg compound,  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$  grade can be mentioned for  $\text{O}_4$ ,  $\text{CoCO}_3$ , and  $\text{Co}(\text{OH})_2$  grade, for example Although it is usually the range of about 650-1000 degrees C, since a still better cycle life is acquired, in the case of 750-900 degrees C, heating temperature is desirable.

[0007]  $\text{A}=\text{Co}$  and  $\text{B}=\text{Mg}$  are [ especially among these ] desirable although it is at least one element chosen from  $\text{A}=\text{Co}$ , at least one element chosen from nickel, Fe, and Cr,  $\text{B}=\text{Mg}$ , and Zn and calcium here. Moreover, although chosen out of the range of  $0 \leq x \leq 0.09$ ,  $0.01 \leq y \leq 0.3$ , and  $0.01 \leq z \leq 0.3$ , the range of  $0 \leq x \leq 0.06$ ,  $0.05 \leq y \leq 0.3$ , and  $0.05 \leq z \leq 0.3$  is desirable, and the range of  $0 \leq x \leq 0.03$ ,  $0.1 \leq y \leq 0.2$ , and  $0.1 \leq z \leq 0.2$  is especially desirable.

[0008] In this invention, a nonaqueous electrolyte rechargeable battery can be created using the above-mentioned positive active material. In this nonaqueous electrolyte rechargeable battery, a negative electrode and the thing usually conventionally used as the electrolytic solution can be used. For example, the nonaqueous electrolyte which

dissolved a lithium, a lithium compound, a lithium alloy, carbon, etc. as a negative electrode, and dissolved the lithium salt of  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{LiPF}_6$  grade as the electrolytic solution into non-aqueous solvents, such as ethylene carbonate (EC), diethylene carbonate (DEC), a propylene carbonate (PC), 1, 2-dimethoxyethane (DME), gamma-butyrolactone (gamma-BL), and a tetrahydrofuran (THF), can be used.

[0009] The method by which the creation method of a nonaqueous electrolyte rechargeable battery is also usually used conventionally is employable as it is. The nonaqueous electrolyte rechargeable battery obtained using the above-mentioned positive active material of this invention has a cycle-life property in outstanding charge and discharge, and as for the cycle life, it has about 1.58 to 1.64 times of about 6 times of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.7}\text{Co}_{0.3}\text{O}_4$ , and  $\text{LiMn}_{1.7}\text{Mg}_{0.3}\text{O}_4$ , and a remarkable effect more than double precision further so that more clearly than the following examples and examples of comparison.

[0010]

[Example] An example and the example of comparison are given to below, and this invention is explained to it. Examples 1-6 and the example 1 of comparison -  $7\text{Li}_2\text{CO}_3$ , electrolysis - After carrying out weighing capacity of  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ , and the  $\text{MgO}$  so that it may become predetermined composition, it mixed with the mortar and the material which calcinates at 900 degrees C for 12 hours, and is shown in Table 1 was compounded. When the powder X diffraction of the obtained material was carried out, as shown in drawing 1 and 2, it has checked that  $2\text{OLiMn}_4$  phase existed. Furthermore, material 0.8g, acetylene black 0.13g, polytetrafluoroethylene 0.07g is kneaded with a mortar and it is thickness. After rolling out to 30 micrometers, you made it stuck to nickel mesh (60mesh) by pressure, 150 degrees C and the vacuum drying of 12 hours were performed, and it used for the cell cycle examination. The thing which stuck diethylene carbonate (DEC) to the electrolytic solution by pressure (ethylene carbonate EC) +50% 1M  $\text{LiClO}_4$ +50%, and made Li foil stick to a counter electrode and a reference pole by pressure on nickel mesh (60mesh) was used. The cell used for the cell examination at drawing 3 is shown. Potential range 3.3-4.3Vvs.Li/Li<sup>+</sup> and current value were made it to 49.4mA per 1g of samples, and temperature was made into 25 degrees C.

[0011] A charge-and-discharge cycle life is shown in Table 1. Whenever Co or Mg replaces a part of Mn in  $\text{LiMn}_2\text{O}_4$  and the amount of substitution increases, a cycle life is large and a bird clapper is known. However, compared with the material which replaced only one element of Co or Mg, a cycle life is still larger and by replacing two elements of Co and Mg simultaneously shows a bird clapper. Furthermore, by carrying out Li substitution, a cycle life is still larger and the material which replaced two elements of Co and Mg simultaneously understands a bird clapper. Thus, by replacing simultaneously a part of Mn in  $\text{LiMn}_2\text{O}_4$  by two elements of Co and Mg or three elements of Li, Co, and Mg rather than it replaces by 1 element independent shows that a cycle life improves further. In addition, a cycle life is made into the life when decreasing to 80% of the service capacity of 1 cycle eye, and says the number of cycles.

[0012]

[Table 1]

		組 成	サイクル寿命 (サイクル数)
比較例	1	$\text{LiMn}_2\text{O}_4$	9 2
	2	$\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$	5 8
	3	$\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$	2 5 0
	4	$\text{LiMn}_{1.7}\text{Co}_{0.3}\text{O}_4$	3 2 0
	5	$\text{LiMn}_{1.9}\text{Mg}_{0.1}\text{O}_4$	7 5
	6	$\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$	2 6 5
	7	$\text{LiMn}_{1.7}\text{Mg}_{0.3}\text{O}_4$	3 3 2
実施例	1	$\text{LiMn}_{1.9}\text{Co}_{0.05}\text{Mg}_{0.05}\text{O}_4$	5 2 5
	2	$\text{LiMn}_{1.8}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	6 0 0 以上
	3	$\text{LiMn}_{1.7}\text{Co}_{0.15}\text{Mg}_{0.15}\text{O}_4$	6 0 0 以上
	4	$\text{Li}_{1.02}\text{Mn}_{1.88}\text{Co}_{0.05}\text{Mg}_{0.05}\text{O}_4$	6 0 0 以上
	5	$\text{Li}_{1.08}\text{Mn}_{1.74}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	6 0 0 以上
	6	$\text{Li}_{1.09}\text{Mn}_{1.71}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	6 0 0 以上

[0013]

[Effect of the Invention] The nonaqueous electrolyte rechargeable battery using the positive active material and this which excelled [ this invention ] in the cycle-life property in charge and discharge can be offered.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[The technical field to which invention belongs] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which were improved.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

PRIOR ART

---

[Description of the Prior Art] A nonaqueous electrolyte rechargeable battery uses a lithium, a lithium compound, a lithium alloy, etc. for a negative electrode, and is a propylene carbonate (PC) as the electrolytic solution. As a positive active material, the sulfide or oxide of transition metals of  $\text{TiS}_2$ ,  $\text{MoS}_2$ ,  $\text{V}_2\text{O}_5$ , and  $\text{V}_6\text{O}_{13}$  grade is mainly used using the nonaqueous electrolyte which dissolved the lithium salt of  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{LiPF}_6$  grade into non-aqueous solvents, such as 1, 2-dimethoxyethane (DME), gamma-butyrolactone (gamma-BL), and a tetrahydrofuran (THF). On the other hand, from the advantage that  $\text{MnO}_2$  used for the nonaqueous electrolyte primary cell is a low cost, it is possible to use this as a positive active material of a rechargeable battery, and it is reported especially that  $\text{LiMn}_2\text{O}_4$  of Spinel structure has the reversibility of charge and discharge.

---

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

EFFECT OF THE INVENTION

---

[Effect of the Invention] The nonaqueous electrolyte rechargeable battery using the positive active material and this which excelled [ this invention ] in the cycle-life property in charge and discharge can be offered.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

 TECHNICAL PROBLEM
 

---

[Problem(s) to be Solved by the Invention] However, in the rechargeable battery using  $\text{LiMn}_2\text{O}_4$  mentioned above as a positive active material, there was a problem that the cycle-life property in charge and discharge was inferior. In order to solve this To for example, JP,2-139861,A The positive active material expressed with  $x(\text{Mn}_{1-z}\text{B}_z)_2\text{O}_4$  A=Na, element B=V chosen from K, Cu, Ag, and Zn, the element  $0.9 \leq x \leq 1.1$  chosen from Cr, Fe, Co, and nickel,  $0.0 \leq y \leq 0.2$ , and  $0.0 \leq z \leq 0.2$ ,  $(\text{Li}_{1-y}\text{A}_y)$  The positive active material which added the divalent metallic ion (for example, Mg, calcium, Zn, Cd) to JP,3-108261,A at  $\text{LiMn}_2\text{O}_4$ , [0004] A part of Mn under  $\text{LiMn}_2\text{O}_4$  crystal is replaced by JP,4-160769,A by Co, and it is from  $\text{Li}_x\text{Mn}_{2-y}\text{M}_y\text{O}_4$  M=Co, and nickel, Fe and Cr. At least one sort of elements  $0.85 \leq x \leq 1.15$  chosen and the positive active material expressed with  $0.3 < y \leq 0.5$  were proposed, and although all were improved, they were not in addition enough. [ of the cycle-life property in the charge and discharge ] The technical problem of this invention is to offer the nonaqueous electrolyte rechargeable battery using the positive active material and this which were excellent in the cycle-life property in charge and discharge.

---

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## MEANS

[Means for Solving the Problem] this invention relates to the nonaqueous electrolyte rechargeable battery using the positive active material and this which are expressed with the following formula.

$\text{Li}_{1+x}\text{Mn}_{2-x-y-z}\text{A}_y\text{B}_z\text{O}_4$  A=Co, at least one element B=Mg chosen from nickel, Fe, and Cr, at least one element  $0 \leq x \leq 0.09$  chosen from Zn and calcium,  $0.01 \leq y \leq 0.3$ ,  $0.01 \leq z \leq 0.3$ . [0006]

[Embodiments of the Invention] One example of the process of a positive active material expressed with the above-mentioned formula of this invention is shown below. For example, the compound expressed with  $\text{Li}_{1+x}\text{Mn}_{2-x-y-z}\text{Co}_y\text{Mg}_z\text{O}_4$  mixes Li compound, Mn compound, Co compound, and Mg compound so that it may become predetermined composition, and it is obtained by heat-treating this mixture. here -- as Li compound --  $\text{Li}_2\text{CO}_3$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and  $\text{LiNO}_3$  grade -- as Mn compound --  $\text{MnO}_2$ ,  $\text{Mn}_3\text{O}_4$ , and  $\text{MnCO}_3$  grade -- as Co compound --  $\text{Co}_3$  -- as a Mg compound,  $\text{MgO}$  and  $\text{Mg}(\text{OH})_2$  grade can be mentioned for  $\text{O}_4$ ,  $\text{CoCO}_3$ , and  $\text{Co}(\text{OH})_2$  grade, for example Although it is usually the range of about 650-1000 degrees C, since a still better cycle life is acquired, in the case of 750-900 degrees C, heating temperature is desirable.

[0007] A=Co and B=Mg are [ especially among these ] desirable although it is at least one element chosen from A=Co, at least one element chosen from nickel, Fe, and Cr, B=Mg, and Zn and calcium here. Moreover, although chosen out of the range of  $0 \leq x \leq 0.09$ ,  $0.01 \leq y \leq 0.3$ , and  $0.01 \leq z \leq 0.3$ , the range of  $0 \leq x \leq 0.06$ ,  $0.05 \leq y \leq 0.3$ , and  $0.05 \leq z \leq 0.3$  is desirable, and the range of  $0 \leq x \leq 0.03$ ,  $0.1 \leq y \leq 0.2$ , and  $0.1 \leq z \leq 0.2$  is especially desirable.

[0008] In this invention, a nonaqueous electrolyte rechargeable battery can be created using the above-mentioned positive active material. In this nonaqueous electrolyte rechargeable battery, a negative electrode and the thing usually conventionally used as the electrolytic solution can be used. For example, the nonaqueous electrolyte which dissolved a lithium, a lithium compound, a lithium alloy, carbon, etc. as a negative electrode, and dissolved the lithium salt of  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ , and  $\text{LiPF}_6$  grade as the electrolytic solution into non-aqueous solvents, such as ethylene carbonate (EC), diethylene carbonate (DEC), a propylene carbonate (PC), 1, 2-dimethoxyethane (DME), gamma-butyrolactone (gamma-BL), and a tetrahydrofuran (THF), can be used.

[0009] The method by which the creation method of a nonaqueous electrolyte rechargeable battery is also usually used conventionally is employable as it is. The nonaqueous electrolyte rechargeable battery obtained using the above-mentioned positive active material of this invention has a cycle-life property in outstanding charge and discharge, and as for the cycle life, it has about 1.58 to 1.64 times of about 6 times of  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.7}\text{Co}_3\text{O}_4$ , and  $\text{LiMn}_{1.7}\text{Mg}_3\text{O}_4$ , and a remarkable effect more than double precision further so that more clearly than the following examples and examples of comparison.

[Translation done.]

## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## EXAMPLE

[Example] An example and the example of comparison are given to below, and this invention is explained to it. Examples 1-6 and the example 1 of comparison -  $7\text{Li}_2\text{CO}_3$ , electrolysis - After carrying out weighing capacity of  $\text{MnO}_2$ ,  $\text{Co}_3\text{O}_4$ , and the  $\text{MgO}$  so that it may become predetermined composition, it mixed with the mortar and the material which calcinates at 900 degrees C for 12 hours, and is shown in Table 1 was compounded. When the powder X diffraction of the obtained material was carried out, as shown in drawing 1 and 2, it has checked that  $2\text{OLiMn}_4$  phase existed. Furthermore, material 0.8g, acetylene black 0.13g, polytetrafluoroethylene 0.07g is kneaded with a mortar and it is thickness. After rolling out to 30 micrometers, you made it stuck to nickel mesh (60mesh) by pressure, 150 degrees C and the vacuum drying of 12 hours were performed, and it used for the cell cycle examination. The thing which stuck diethylene carbonate (DEC) to the electrolytic solution by pressure (ethylene carbonate EC) +50% 1M  $\text{LiClO}_4$  +50%, and made Li foil stick to a counter electrode and a reference pole by pressure on nickel mesh (60mesh) was used. The cell used for the cell examination at drawing 3 is shown. Potential range 3.3-4.3V vs.  $\text{Li/Li}^+$  and current value were made it to 49.4mA per 1g of samples, and temperature was made into 25 degrees C.

[0011] A charge-and-discharge cycle life is shown in Table 1. Whenever Co or Mg replaces a part of Mn in  $\text{LiMn}_2\text{O}_4$  and the amount of substitution increases, a cycle life is large and a bird clapper is known. However, compared with the material which replaced only one element of Co or Mg, a cycle life is still larger and by replacing two elements of Co and Mg simultaneously shows a bird clapper. Furthermore, by carrying out Li substitution, a cycle life is still larger and the material which replaced two elements of Co and Mg simultaneously understands a bird clapper. Thus, by replacing simultaneously a part of Mn in  $\text{LiMn}_2\text{O}_4$  by two elements of Co and Mg or three elements of Li, Co, and Mg rather than it replaces by 1 element independent shows that a cycle life improves further. In addition, a cycle life is made into the life when decreasing to 80% of the service capacity of 1 cycle eye, and says the number of cycles.

[0012]

[Table 1]

		組 成	サイクル寿命 (サイクル数)
比較例	1	$\text{LiMn}_2\text{O}_4$	9 2
	2	$\text{LiMn}_{1.9}\text{Co}_{0.1}\text{O}_4$	5 8
	3	$\text{LiMn}_{1.8}\text{Co}_{0.2}\text{O}_4$	2 5 0
	4	$\text{LiMn}_{1.7}\text{Co}_{0.3}\text{O}_4$	3 2 0
	5	$\text{LiMn}_{1.9}\text{Mg}_{0.1}\text{O}_4$	7 5
	6	$\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$	2 6 5
	7	$\text{LiMn}_{1.7}\text{Mg}_{0.3}\text{O}_4$	3 3 2
実施例	1	$\text{LiMn}_{1.9}\text{Co}_{0.05}\text{Mg}_{0.05}\text{O}_4$	5 2 5
	2	$\text{LiMn}_{1.8}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	6 0 0 以上
	3	$\text{LiMn}_{1.7}\text{Co}_{0.15}\text{Mg}_{0.15}\text{O}_4$	6 0 0 以上
	4	$\text{Li}_{1.02}\text{Mn}_{1.88}\text{Co}_{0.05}\text{Mg}_{0.05}\text{O}_4$	6 0 0 以上
	5	$\text{Li}_{1.08}\text{Mn}_{1.74}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	6 0 0 以上
	6	$\text{Li}_{1.09}\text{Mn}_{1.71}\text{Co}_{0.1}\text{Mg}_{0.1}\text{O}_4$	6 0 0 以上

[Translation done.]

\* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1] It is the X diffraction view of the positive active material obtained in  $\text{LiMn}_2\text{O}_4$  and the examples 1-3.

[Drawing 2] It is the X diffraction view of the positive active material obtained in  $\text{LiMn}_2\text{O}_4$  and the examples 4-6.

[Drawing 3] The cell used for the charge-and-discharge cycle examination is shown.

---

[Translation done.]

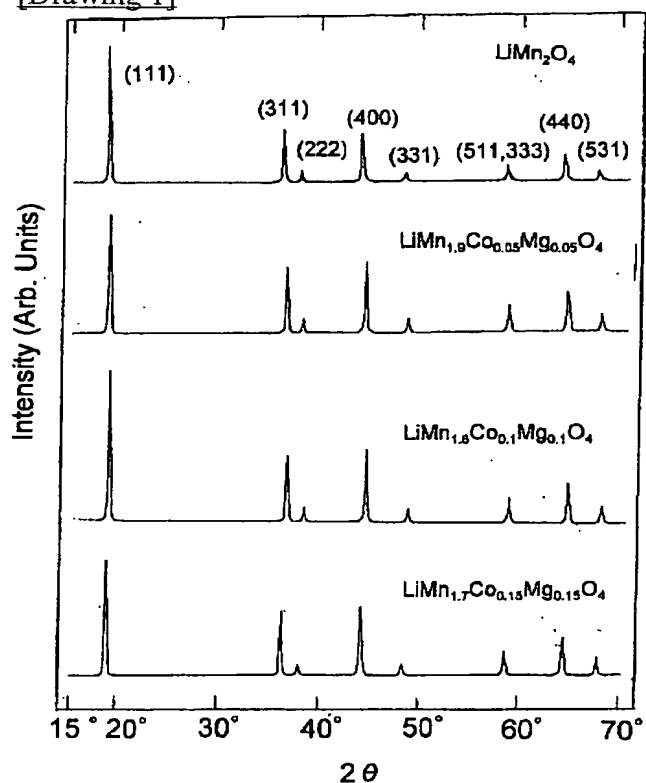
## \* NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

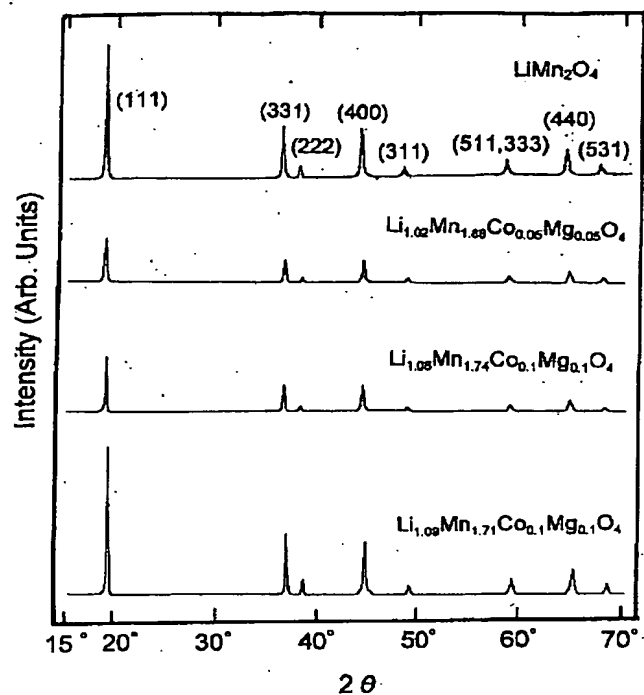
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## DRAWINGS

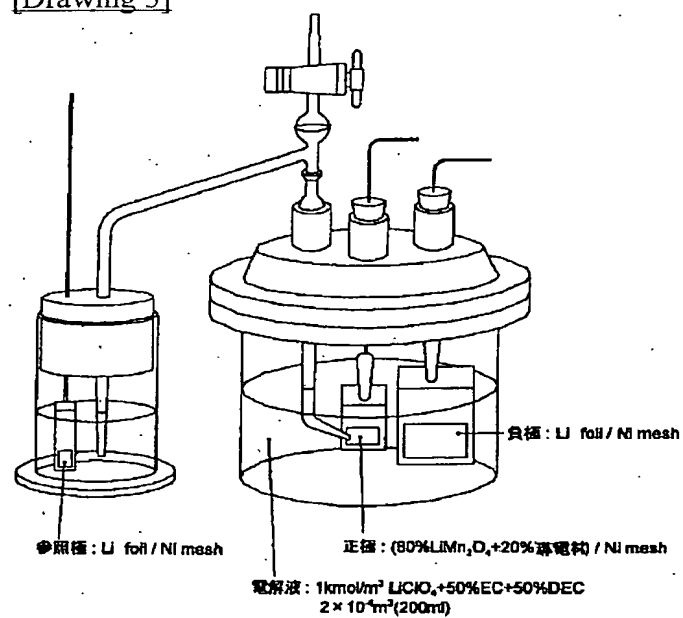
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]